

Investigations on Carbonaceous Airborne Particulate Matter with STXM

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Beamline: X1A

Introduction: We present the first results of an investigation of the molecular structure of carbon in diesel particulate matter (DPM) by STXM. The DPM samples were produced in a small diesel engine test facility at the University of Utah equipped with extensive online monitoring apparatus. It is demonstrated that one can discriminate and localize aromatic and aliphatic groups in single DPM particles and distinguish unburned fuel and oil from solid soot.

Methods and Materials: Conventional diesel was combusted in a test engine, and the soot particles were collected on a filter following the exhaust. Part of the soot was removed from the filter, immersed in acetone and then one drop of this solution was placed on a Si_3N_4 window for further analysis in the STXM. STXM experiments were carried out beamline X1A at the National Synchrotron Light Source in Brookhaven National Laboratory [3]. Scans with a lateral resolution of 50 nanometer were taken at X-ray energies that ranged from 280 eV to 293 eV, in steps of 0.05 eV. Thus, a stack of 280 images, each at a different X-ray energy, is obtained. The data analysis program, based on IDL programming language, provides graphic tools to single out regions of particular interest.

Results: Figure 1 displays a STXM micrograph (left picture) of an area of approximately $10\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$, obtained at an X-ray energy of 284.6 eV. Micrographs were scanned at energies between 280 and 293 eV, in steps of 0.1 eV. The micrograph includes an inset of a magnified region with one single particle that we have studied. To the right, in Figure 1, a series of carbon K-edge absorption spectra is shown. They were obtained from the single particle shown in the inset. The carbon K-shell absorption edge is located at about 283 eV. At about 285 eV, we find the $\pi_{1,2}$ transition, while the somewhat less pronounced peaks at 288 eV are termed $\pi_{3,4}$. The π resonance at 285 eV is indicative of a transition from a 1s state to a 1p state and is observed for molecules with carbon double bonds and triple bonds. The spectra allow for the discrimination between carbon in aromatic and aliphatic bonding conditions. Using conventional X-ray near edge absorption spectroscopy (XANES), or XRD, one can make a only global distinction between the aromatic and aliphatic partitions in the carbon sample. With the use of STXM, however, we are able to trace back locations with more graphitic or more amorphous carbon. The STXM data analysis software allows one to select specific single regions in the micrograph and to obtain the corresponding XANES spectra. We have selected one such particle as shown in Figure 1. The particle was encircled, and the transmitted intensity of the circle line was defined as the background signal I_0 . The inset shows how the particle was encircled (highlighted pixels which build the circle) and how the center of the particle was selected (highlighted pixel in center). From the ratio of both intensities, the X-ray optical density (μd) of the particle center was determined: $I_p = I_0 \cdot \exp(-\mu d)$. This procedure yields the XANES spectrum of one particle region, and a whole set of such spectra from different regions of one particle are shown on the right side of Figure 1.

In the next step, the pixel in the center of the particle was encircled by the smallest possible pixel circle, while the center pixel itself was omitted. The summarized intensity of this circle was taken I_p , while I_0 was not changed. This procedure yields the second XANES in a series of seven XANES, and finally allows us to build a line profile scan across the entire particle. In the next stage of analysis, the heights of the $\pi_{1,2}$ and $\pi_{3,4}$ transitions were determined and their ratio was formed. This ratio is plotted versus the radius of the circles of data gathering in the inset in figure 2. The curvature of the ratio versus the distance from the sample center shows that the particle center is made of carbon with predominantly $\pi_{1,2}$ transitions. The boundary probably contains more aliphatic carbon (residual fuel, lubricant), which was washed out from the particle when the sample was prepared with acetone.

In Figure 2, we see a micrograph of a different sample region, taken at an X-ray energy of 285.11 eV. The images show inhomogeneities (bright, on dark background), which can be assigned with soot particles of a size smaller than one micrometer. The background intensity I_0 is recorded in the upper right corner (marked dark), and the transmitted intensity I_p is marked bright. In the left micrograph, the region of interest is the wash-out corona around some particles, this is, a region around the sample where washed out residual fuel and oil are located. As an inset in the image, the optical density (the logarithm of the bright region intensity I_p divided by the dark region intensity I_0) is shown versus the X-ray energy. The micrograph on the right displays the same X-ray image, but now only the cores (bright dots) of particles are selected for analysis. The corresponding XANES spectrum shows peaks at exactly the same positions as the wash out corona does. However, peak intensity ratios are quite different. The washed out region has a pronounced $\pi_{3,4}$ transition peak, while the particle centers have a pronounced $\pi_{1,2}$ transition peak.

The carbonaceous soot particles are very likely porous aggregates and loaded with residual fuel and lubricant. Immersed in acetone and then poured on a sample slide, a corona can be found around the particles.

Conclusions: We have demonstrated that we can single out particular particles and particle regions of interest with STXM and analyze them for the type of carbon present. Due to the chemical contrast, we are able to distinguish between aromatic and aliphatic types of carbons and can assign them to particular sample regions. Our next step will be to collect a set of reference spectra from materials, which are important for diesel combustion; those include commercially available diesel, lubricants, additives, as well as model substances such as octane and hexadecane. We anticipate that STXM will enable us to get a more detailed picture about the spatial distribution of species in DPM.

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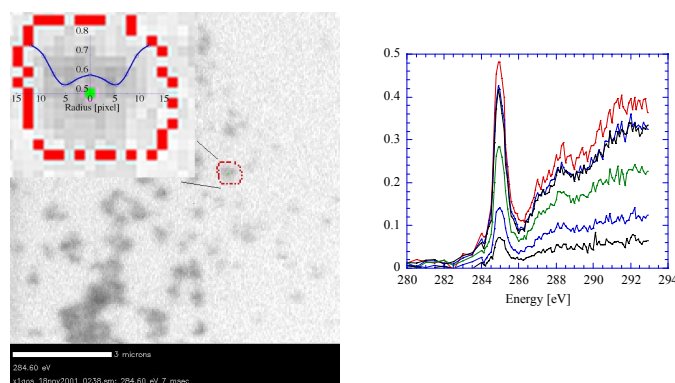


Figure 1: Left - STXM micrograph with particles dispersed on Si_3N_4 window. Inset with magnified single particle and imprinted differential concentration profile. Right – series of carbon K-edge XANES from different regions on one particle

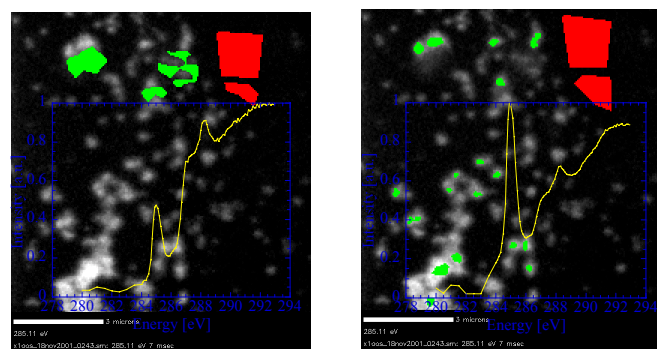


Figure 2: Left – XANES of material in particle boundary, pasted on STXM image. Right XANES of material in particle center, pasted on STXM image.